Modification of Activated Carbon Derived from Cyperus Papyrus Plant

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Abstract: Activated carbon from papyrus plant was prepared by the chemical activation with sulfuric acid 3:1 (wt./wt.). The prepared activated carbon then burning at 600°C under N_2 atmosphere for 2 h. The produce coded AC_0, further modification of AC_0 by using different oxidizing and reducing solutions. The solutions were a (mixture $NaNO_3$ with $KMnO_4$ in 10% H_2SO_4 coded (AC_1) 10% $ZnCl_2$ coded (AC_2) 10% $NaBH_4$ coded (AC_3) 10% HNO_3 coded (AC_4). Characterization properties for the prepared activated carbons (AC_0-AC_4) were accomplished using techniques including FTIR, SEM, XRD, TGA and BET. BET showed a substantial increase in the surface area of AC_2, AC_3, accompanied by reduced intensities of certain IR vibrations (1720, 3420 cm^{-1}) as well as absence of pronounced peak at $2\theta = 25$ in XRD. While samples prepared by the treatment with oxidizing reagent showed a noticeable increase in the intensity of IR band at 3420 cm^{-1} as well as emergence of vibration band at 1720 cm^{-1}. Moreover, the peak at $2\theta = 25$ were showed an increase in the intensity. The pore volume showed variable behavior depending on the type of the reagent used for the treatment. However, the pore volume increased by the treatment with $NaBH_4$ and decreased by the treatment with $NaNO_3$/$KMnO_4$ solution. The TGA thermographs were with a good accordance with pore volume indicating a high carbon percentage more than 82% by the end of heating cycle and departure of volatile hydrocarbons as a result of treatment with reducing agents particularly $NaBH_4$ right from the beginnings.

Key words: Activated carbon, modified active carbon, sulfuric acid, papyrus plant, particularly, emergence

INTRODUCTION

Activated carbon is one of the materials widely used in water treatment due to its excellent adsorbent properties, microporosity, high surface area and valiable corrosion resistance. Generally, preparation of activated carbon is classified into physical activation and chemical activation. Since, chemical activation usually takes place at shorter time and a lower temperature needed for activating the materials. The chemical activation costs less. The most studied chemical activation parameters are, temperature, time and impregnation ratio (activating agent/precursor). The activation time has little influence on the process. In contrast, impregnation ratio and activation temperature are very significant. In general, the increase in the activation temperature leads to a decrease in yield and an increase in the surface area. The impregnation ratio shows a similar conduct, however, the yield reduce is less pronounced and larger surface areas are gained. AC with high surface area and large yields are obtained at activation temperatures about 500°C (Mahamad *et al.*, 2015; Ozsgn, 2011). In chemical activation, the main activating agents used are $ZnCl_2$ (Mahmoudi *et al.*, 2014), KOH (Arie, 2016), NaOH (Pandey *et al.*, 2016), K_2CO_3 (Buczek, 2016), H_2SO_4

(Gomes *et al.*, 2010) and H3PO4 (Ozsgn, 2011). Taking into account their environmental impact and the possibility of their return, $ZnCl_2$ is the most preferred compound. Several researchers have reported the preparation activated carbon of chemically activated carbons from many types of raw materials as, for example, from lignine (Yangui, 2013) sawdust (Abdel-Ghani *et al.*, 2016) rice (Pandey *et al.*, 2016) bagasse fly ash (Baghel *et el.*, 2011) olive-waste cakes, olive stones. Dates pits (Amor *et al.*, 2015; Erabee *et al.*, 2017) were chosen to prepare the activated carbon successfully because of their high cellulose fiber content. A high surface area and an sufficient pore size distribution are very important for the activated carbon to executed well in the adsorption application. However, activated carbon with similar porous characteristics may show a very changes adsorption capacity with the same adsorbantes. This is due to the porous structure influences the optimization of the adsorption capacity of activated carbon. The amount and the nature the of the surface functional groups present in the activated carbons surface taken into account. Surface functional groups of carbon materials directly depend on the precence of heteroatoms such as oxygen, nitrogen and other atoms and inorganic ash components that may come from the carbon raw materials or activating agent.

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The main object of this study was the synthesis of a higher value activated carbon from papyrus plant via. chemical activation with H_2SO_4 (AC_0). In addition, further modification to the surface chemistry of activated carbon by using some regents such as $NaNO_3/KMnO_4$ solution coded (AC_1) $ZnCl_2$ coded (AC_2) $NaBH_4$ coded (AC_3) and HNO_3 coded (AC_4). The samples were tested using BET, TGA, XRD, SEM and FTIR spectroscopy.

MATERIALS AND METHODS

Preparation of activated carbon: The papyrus plants were collected from the shores of the Euphrates River which is located 15 km North-West of the city of Samawah Southern Iraq. The papyrus plant was washed with distilled water and dried at (80-105°C) thenplants were cut to small pieces and crushed to coarse grains (El-Wakil *et al.*, 2015). The prepared samples soaked in sulfuric acid solution (wt./wt.) 3:1, 48 h and then separated by decantation, washed by distilled water and dried at 105°C. The dried sample transported into a quartz container and covered with aluminum foil then covered with a layer of graphite powder to avoid oxidation. The container was placed in a muffle furnace and the sample were heated to a temperature of 600°C and kept at this temperature for 2 h under N_2 atmosphere. The produced carbon was cooled dawn and washed with distilled water until pH = 7. This carbon coded AC_0 (Tan *et al.*, 2008; Ahmadpour and Do, 1996; Hesas *et al.*, 2013).

Modification of activated carbon

Treatment with oxidation reagents: The used reagents involved are $NaNO_3/KMnO_4$ a solution and 10% nitric acid in this part to oxidation surface activated carbon (El-Wakil *et al.*, 2015). Socking 20gm from activated carbon AC_0 with Hummer's solution in 250 mL conical flask for 2 h with stirring by magnetic bar at temperature of 40°C. The sample then filtered and washed with distilled water, then dried at 105°C this carbon called (AC_1) and socked 20 g from AC_0 with nitric acid 10%-2 h with stirerring at 40°C then filtered and washed and dried at 105°C to produce AC_4 (Babatunde *et al.*, 2016; Zielke *et al.*, 1996).

Treatment with reduction reagents: The used reagents involved are solution from 10% $ZnCl_2$ and 10% $NaBH_4$ to reduce the surface activated carbon. Socking 20 g from AC_0 in solution $ZnCl_2$ 10% and 20 g from AC_0 in solution $NaBH_4$ 10% in 250 mL conical flask to 2 h with stirring by magnetic bar at temperature 40°C, then filtered and washed with distilled water and dried at 105°C. the activated carbon treated with $ZnCl_2$ 10% coded AC_2 and activated carbontreated with $NaBH_4$ 10% coded AC_3.

Characterization techniques: Thesurface functional groups ofthe prepared activated carbon (AC_0-AC_4) were obtained by the Fourier Transform Infrared spectroscopy (FTIR) over the range of 400-4000 cm^{-1} using a (Shimadzu) FTIR instrument. The microstructure of the samples was examined using a Scanning Electron Microscope (SEM, Bruker-Nano-GMbH-Germany). The carbons surface properties were determined with an automatic adsorption instrument (ISO\IEC 17025-QSURF surface area analyzer) in order to determine surface areas and total pore volumes. Thermogravimetric analysis of thecarbons was also, carried out using a Thermogravimetric Analyzer (PerkinElmer-TGA-4000). X-Ray Diffraction (XRD) patterns were recorded on a (Shimadzu-XRD-6000-Japan) with CuKα radiation (λ = 1.5406 Å).

RESULTS AND DISCUSSION

FTIR spectroscopy analysis: Figure 1 and 2 illustrate the IR spectra of the samples (AC_0-AC_4). They show the difference between untreated carbon and treated carbon. In general, oxygen functional groups are formed and disappeared according to each particular reagent. All samples show a hydroxyl group vibration in the range of (3383-3446 cm^{-1}) but the OH group is rather intense for samples treated with oxidizing agent Fig. 1 in comparasion with samples treated with reducing agents Fig. 2. The bands in the region (1706-1714 cm^{-1}) shown in the carbon spectrum (AC_1, AC_4) are due to the vibration of the carbonyl group (aldehyde ,lactone, carboxyl) groups (Zielke *et al.*, 1996). The bands are near the region (1500-1650 cm^{-1}) due to the vibration of the group (C = C) in the aromatic rings. The bands shown in the region (1220-1240 cm^{-1}) are due to the vibration of the (C-O) group of the ethers and alcohols. The apparent bands in the region of 610-875 cm^{-1} are due to the out plane ring deformation in C = C bonds. The disappearance of bands in the region (1704-1714 cm^{-1}) for carbon (AC_2, AC_3) is due to the reduction of carbonyl groups and their conversion into carboxyl or ethylene groups and the appearance of carbonyl groups in the carbon spectrum (AC_1, AC_4) due to oxidation of the surface groups by oxidizing agents.

Scanning Electron Microscopy (SEM) the Scanning Electron Microscopic (SEM) images of the unmodified AC_0 and modified activated carbons (AC_1-AC_4) showed in Fig. 3a-c. The SEM enables the direct observation of the changes in the surface microstructures of the carbons due to the modification. A ruptured surface with long ridges resembling a series of parallel lines and a small number of pores. The chemical activation with reduction reagents allowed the development of pores with different sizes on the carbon surface (Candelaria *et al.*, 2012). As can be
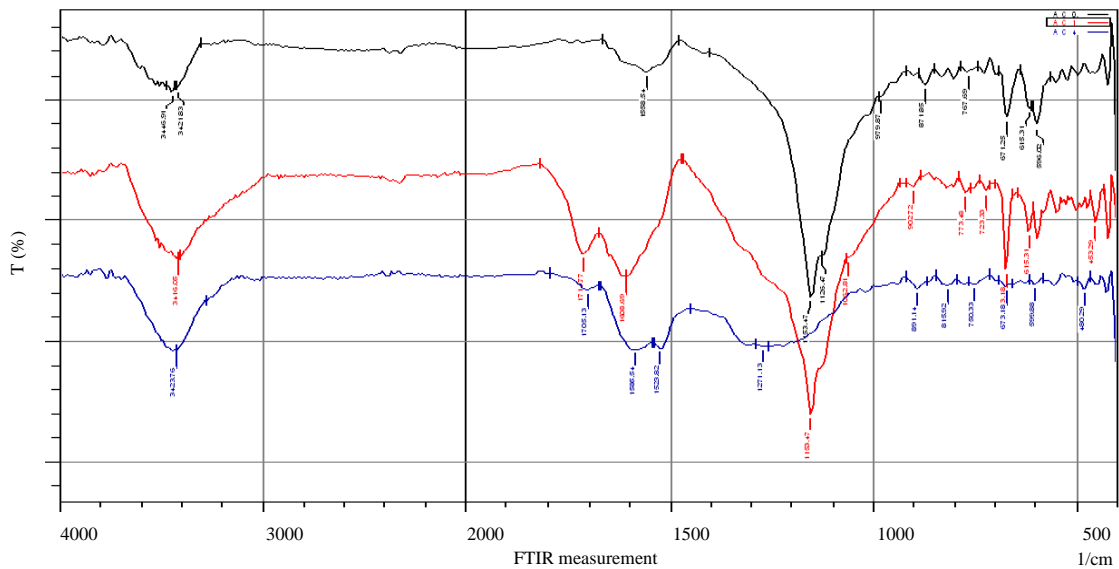
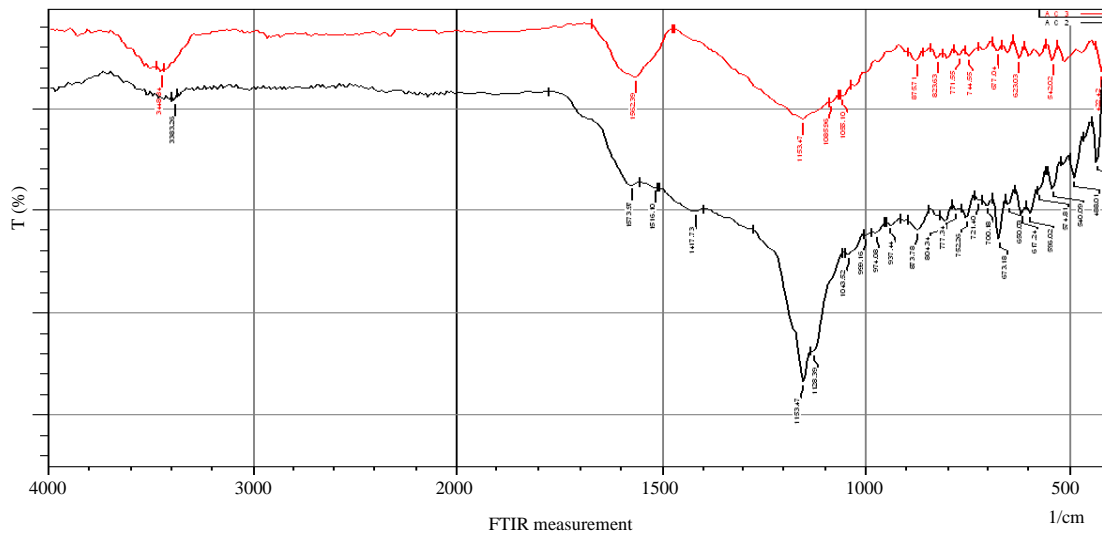Fig. 1: FTIR spectra for AC_0, AC_1, AC_4

Fig. 2: FTIR spectra for AC_3, AC_2

seen from Fig. 3a, d a number of small sized pores have been developed on the surface of AC_1. The surface of AC_2, AC_3; Fig. 3c, d illustrate large pores, nonhomogenous in size and randomly distributed on the carbon's surface. Large and well-developed pores were clearly found on the surface of the activated carbon AC_3 as seen in Fig. 3d. It can be concluded that surface modification by reducing solution of papyrus contributed positively to the pores development.The chemical activation with oxidation reagents as Fig. 3b, e showed conglomerates in activated carbon particles on surface due to attraction positive charges with negative charges (Candelaria *et al.*, 2012; Jahangiri *et al.*, 2012).

Thermogravimetric Analysis (TGA): TGA analysis of the activated carbons was obtained by heating the samples from 50-750°C at a ramping rate of 10°C/min under helium gas atmosphere. The TGA curves of the different activated carbons prepared from papyrus plant are presented in Fig. 4. At temperatures above 100°C, chemical bonds begin to break. The rate at which the bonds are broken increases as the temperature increases. The weight loss from room temperature to 130°C observed in the thermographs corresponds to the release of water vapor. Upon rapid heating, the carbohydrates (cellulose and hemicellulose) break down to provide low molecular weight volatile products. Another weight loss step
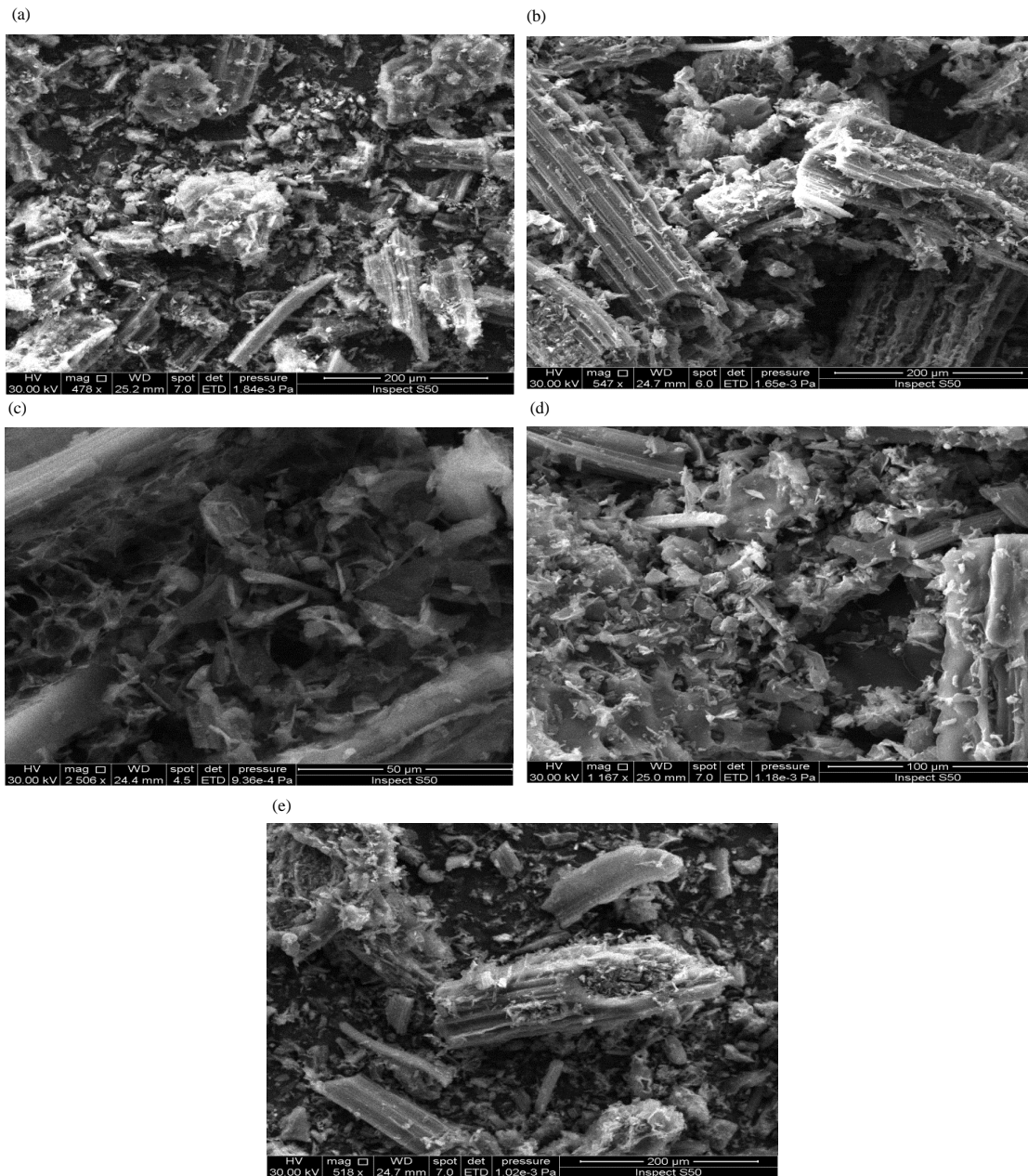
(a)

(b)

(c)

(d)

(e)

Fig. 3: SEM photo for: a) AC_0; b) AC_1; c) AC_2; d) AC_3 and e) AC_4

occurred from above 100°C to around 400°C. This step was attributed to the removal of volatile matter which corresponded to the decomposition of cellulose, hemicellulose and lignin. The broad weightloss step thatoccurs above 350°C is due to carbonization process which may be attributed to cellulose, hemicellulose andlignin intermediates being transformed to gaseousmaterials and tars. The observedweight loss taking place at temperatures near 750°C might be due to a possible melting of the traces of carbonate, contained in

the carbon matrix,and its possible decomposition into CO_2. The carbon thermal stability of the carbon samples (AC_0-AC_4) were different with the percentage of the remaining weight of carbon AC_0 being 88% and the carbon treated with oxidizing reagents AC_1, AC_4 was 72.79 and 80.26%, respectively, due to the formation of oxygen functional group on the surface due to the treatment and volatilization led to a loss in the weight of carbon AC_1, AC_4. The percentage of the carbon is treated with reduced agents AC_2, AC_3 remaining weight was 82.5, 88.4% and
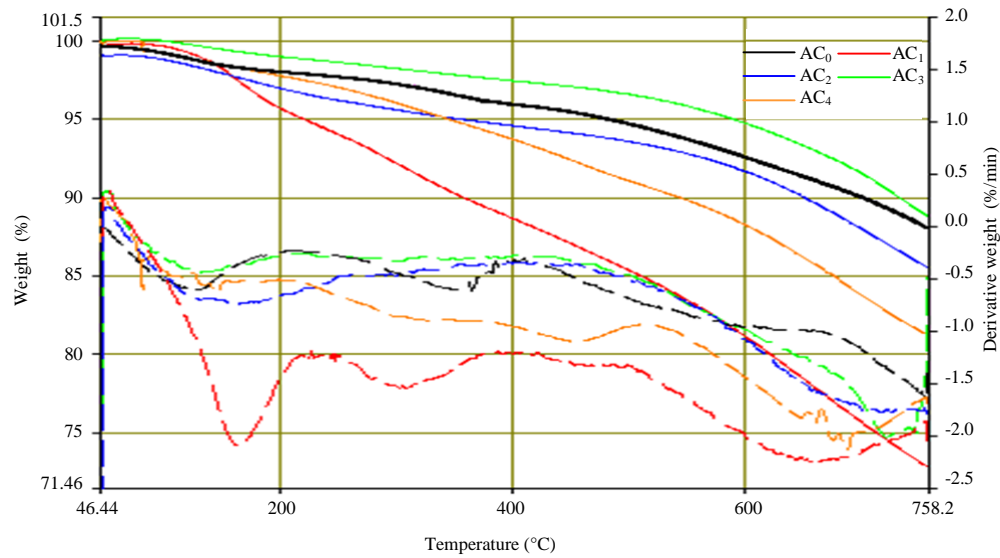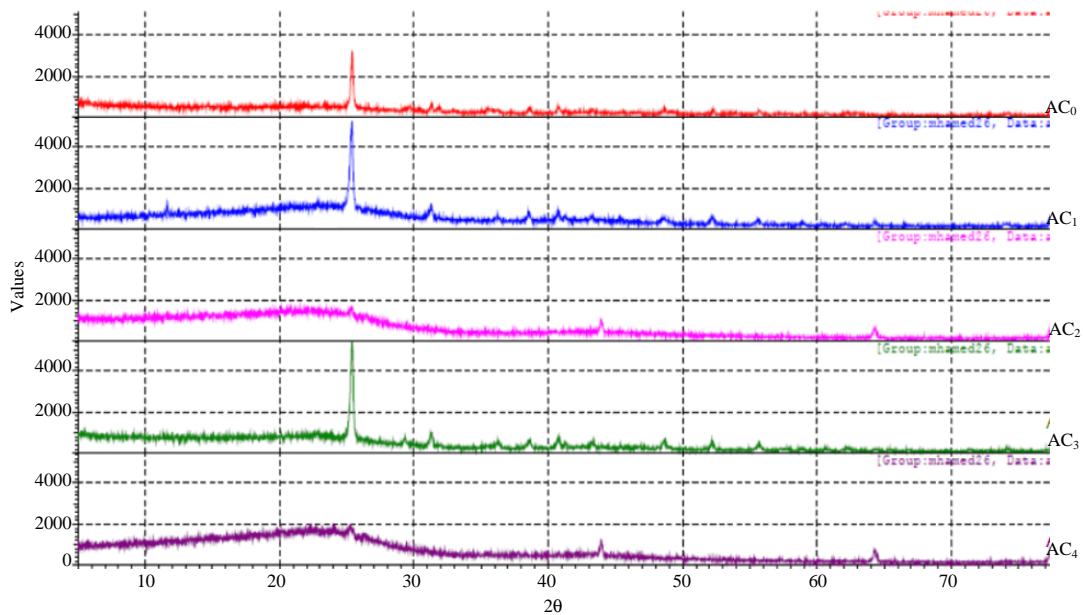
Fig. 4: TGA analysis for (AC$_0$-AC$_4$)

Fig. 5: XRD analysis for (AC$_0$-AC$_4$)

the stability was increased. The reason for the activation step was that some groups were reduced to volatile compounds which increased the carbon ratio in samples AC$_2$, AC$_3$ and increased its stability in higher temperatures.

X-ray diffraction analysis: Figure 5 shows the X-ray diffraction spectra of activated carbon untreated, treated with oxidizing reagents AC$_1$ and AC$_4$ and the reduced reagents AC$_2$ and AC$_3$ where, the untreated activated carbon shows a diagnostic peak at 2θ = 25 for the

crystalline structure of activated carbon because it has a crystallization ratio graphite. The activated carbon spectra treated with oxidizing reagents AC$_1$ and AC$_4$ shows a similar carbon-like spectrum with an increase in intensity at 2θ = 25.419. This indicates a more uniformity of the crystalline shape and reduced deformation, leading to a decrease in surface area as proven by BET measurements (Rakovan, 2004).

The X-ray diffraction spectra of the carbons treated with reduced reagents AC$_2$ and AC$_3$ showed a significant difference from the carbon spectrum AC$_0$. The spectra

Table 1: Showed surface area and pores volume for (AC_0-AC_4)

Activated carbon types	AC_0	AC_1	AC_2	AC_3	AC_4
Surface area (m^2/gm)	199.767	4.1016	275.328	330.693	137.687
Pore volume (cm^3/gm)	0.1689	0.0649	0.1298	0.1843	0.1158

showed a broad band indicate significant reduction in carbon AC_2 and AC_3 due to the reduction of some functional groups and their volatilization in volatile hydrocarbons, leaving voids in the crystalline network that distort the crystal structure of carbon AC_0 increasing surface area as proven by BET analysis.

Surface area and pores volume analysis (BET): Analysis of surface area of untreated activated carbon AC_0 showed a surface area of 199,767 m^2/g and a pore volume of 0.1689 cm^3/g. Activated carbon, treated with oxidizing reagents AC_1 and AC_4, gave a surface area less than the surface area of carbon AC_0. The carbon AC_0 was 4.1016 m^2/g, pore size was 0.0649 cm^3/g, carbon AC_4 was 137.687 m^2/gandpore size was 0.1158 cm^3/g, due to aggregations on activated carbon surface AC_1 and AC_4 due to the attraction of different charges in the surface area as well as increased regulation of the crystalline network as in the analysis of X-ray diffraction led to a decrease of surface area.

The surface area of activated carbon treated with reduced reagents AC_2 and AC_3 increased significantly from the surface area of activated carbon AC_0 and an increase in the volume of carbon AC_3 pores. The surface area of carbon AC_2 was 275.328 m^2/g, the volume of the pores was 0.1298 cm^3/g, the carbon AC_3 was 330.693 m^2/g and the volume of the pores was 0.1843 cm^3/g. This is due to the reduction of some active groups on the surface carbon and their transformation into volatile hydrocarbons during the activation stage, leaving porous structures in the crystalline network increasing the carbon area AC_2 and AC_3. The increased pore size of carbon AC_3 is due to the broken walls between the small pores and turning into larger pores. The decrease in pore size of carbon AC_2 indicates new pores as well as the original pores (Table 1).

CONCLUSION

The possibility of using materials available locally such as papyrus available in large quantities in the southern region to produce activated carbon by concentrated sulfuric acid at low cost and high efficiency. The possibility of altering the surface of activated carbon prepared by using reducing agents such as zinc chloride and sodium borohydride to increase surface area of activated carbon and improve adsorption properties.

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